Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 5503–5507 **5503**
DOI: 10.1021/ma1009275

Cationic Polymerization of Isobutylene Using $AlCl_3OBu_2$ as a Coinitiator: Synthesis of Highly Reactive Polyisobutylene

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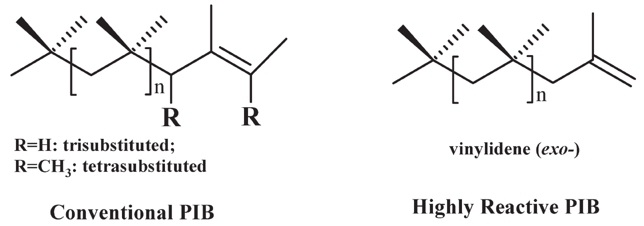
Received April 27, 2010
Revised Manuscript Received May 25, 2010

Introduction. Low molecular weight polyisobutylenes (M_n = 500−5000 g mol^{-1}) are one of the most important industrial representatives of isobutylene polymers, which are used as intermediates in the preparation of additives for lubricants and fuels.[1,2] Components for these additives are prepared by reacting the double-bond-terminated polyisobutylenes with maleic anhydride.[3] Currently, two chemically distinct processes, $AlCl_3$- and BF_3-catalyzed polymerization of isobutylene, are commercially used for the synthesis of double-bond-terminated polyisobutylenes.[3,4] The so-called conventional polyisobutylene (PIB), which contains up to 90% of internal double bonds (trisubstituted, tetrasubstituted, see Scheme 1), is industrially produced by $AlCl_3$-catalyzed polymerization of isobutylene.[4] Since internal double bonds are characterized by low reactivity to maleic anhydride, the conversion of polyisobutylene to corresponding diene through the chlorination−dehydrochlorination procedure before its reaction with maleic anhydride is required.[4] This leads to large quantities of chlorine-containing waste. On the other hand, a high content of the vinylidene end groups (*exo*-olefin end groups, Scheme 1) would be strongly desired since they react at a sufficiently high rate with maleic anhydride. These polyisobutylenes, also called highly reactive polyisobutylenes, contain 75−85% of *exo*-olefin end groups and are commercially available from BASF.[5]

Market prognoses clearly indicate that the production of highly reactive polyisobutylene will increase in the coming years and higher quality products (higher content of *exo*-olefin terminal groups, narrower molecular weight distribution, etc.) will be needed.[6] Therefore, considerable attention has been paid recently to new initiating systems for the synthesis of highly reactive polyisobutylene. Ivan et al.[7] proposed a two-step process for the preparation of mono- or difunctional *exo*-olefin-terminated PIB (95−98% of *exo*-olefin groups), which involved the synthesis of *tert*-chloride-terminated PIB at −78 °C via controlled cationic polymerization followed by dehydrochlorination of isolated polymer with excess of potassium *tert*-butoxide in refluxing tetrahydrofuran for 24 h. Telechelic polyisobutylene with ~100% of *exo*-olefin groups can also be obtained by the reaction of *tert*-chloride-terminated PIB with isobutenyltrimethylsilane in the presence of $TiCl_4$ at −78 °C.[8] Quantitative formation of *exo*-olefin-terminated PIB (95−100%) by end-quenching $TiCl_4$-coinitiated living isobutylene polymerization with such hindered bases as 2,5-dimethylpyrrole or 1,2,2,6,6-pentamethylpiperidine at −40 to −60 °C was recently reported by Storey et al.[9] The same author reported an alternative way toward polyisobutylene with *exo*-olefin terminal bond (69−97%) consisting in the formation of an adduct between sulfide and living polyisobutylene at −60 °C followed by the adduct decomposition by excess of nucleophile (methanol, triethylamine, 2,6-di-*tert*-butylpyridine).[10] From a practical point of view, the main drawbacks of the above-mentioned processes are (i) low reaction temperatures, (ii) use of expensive reagents, and (iii) (often) multistep procedures.

Scheme 1. Chain-End Structures of Conventional and Highly Reactive PIB



Quite recently, it was shown that solvent-ligated complexes of the general formula $[M(NCCH_3)_6](A)_2$ (M = Mn,[11] Mo,[12] Cu;[6,13] A = noncoordinating borate anions) induced cationic polymerization of isobutylene to afford highly reactive polyisobutylenes (60−95% of *exo*-olefin groups) with molecular weight between 300 and 13 000 g mol^{-1} and reasonable molecular weight distribution (M_w/M_n = 1.4−3.0) at elevated temperatures (20−60 °C).[6,11−14] However, these complexes are currently too expensive to be of significant interest for industry. Heteropolyacids of the formula $(NH_4^+)_{2.5}H_{0.5}PW_{12}O_{40}$ were recently shown to polymerize isobutylene at −5 °C into highly reactive polyisobutylene (70−85% of *exo*-olefin groups) with M_n = 1000−3500 g mol^{-1} but with very broad molecular weight distribution (M_w/M_n = 5−25).[4] An interesting and simple initiating system, *tert*-butyl chloride/EtZnCl, was used for the synthesis of medium molecular weight (M_n = 10 000−29 000 g mol^{-1}) polyisobutylenes with *exo*-olefin terminal groups at 20 °C.[15] However, a high content of vinylidene end groups (85−92%) was observed only at low conversions (< 30%), while only 60% of *exo*-olefin terminal groups were detected at ~95% of monomer conversion.[15]

We recently reported for the first time an $AlCl_3$-based initiating system, 2-phenyl-2-propanol (CumOH)/$AlCl_3OBu_2$, for the controlled cationic polymerization of styrene.[16] Motivated by these results, we extended our study to the polymerization of isobutylene. We report here the application of the CumOH/$AlCl_3OBu_2$ initiating system to the synthesis of highly reactive polyisobutylene containing 86−95% of *exo*-olefin end groups. The aim of this work is to develop an efficient and cheap initiating system for the synthesis of highly reactive PIB, which meets the following criteria: (i) content of *exo*-olefin terminal groups ≥ 90%; (ii) $M_n \leq 3000$ g mol^{-1}; (iii) $M_w/M_n < 2.0$; (iv) reaction time ≤ 10 min; (v) polymerization temperature > −40 °C.

Results and Discussion. Table 1 summarizes the results of our investigations on the cationic polymerization of isobutylene using $AlCl_3$-based initiating systems. At low initiator concentration, the CumOH/$AlCl_3OBu_2$ initiating system induced slow cationic polymerization of isobutylene (conversion = 47% for 30 min), affording polymers with high content of vinylidene end groups (95%); however, only 37% of

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Table 1. Cationic Polymerization of Isobutylene with CumOH/$AlCl_3ED$ Initiating System (ED = Bu_2O, Ph_2O, EtOAc)[a]

run	CumOH (mM)	coinitiator (mM)	T (°C)	conv (%)	M_n (g mol^{-1})	M_w/M_n	*exo*-olefin (%)	F_n[b] (%)
1[c]	3	$AlCl_3OBu_2$ (22)	−60	47	3510	1.93	95	37
2	18	$AlCl_3OBu_2$ (22)	−60	85	2330	1.81	86	91
3	18	$AlCl_3OBu_2$ (22)	−40	62	1560	1.46	91	75
4[d]	18	$AlCl_3OBu_2$ (22)	−40	60	1490	1.38	93	56
5[e]	18	$AlCl_3OBu_2$ (22)	−40	37	1270	1.17	93	48
6	36	$AlCl_3OBu_2$ (44)	−40	73	1200	1.20	90	91
7	18	$AlCl_3OBu_2$ (22)	−20	49	1150	1.16	91	65
8[f]		$AlCl_3OBu_2$ (22)	−20	46	1750	2.25	92	
9	6	$AlCl_3OPh_2$ (7.5)	−20	100	2020	3.94	–[g]	7
10	18	$AlCl_3$0.7EtOAc (22)	−20	50	1810	1.86	53	57
11	10	$AlCl_3$ (7.5)	−20	60	2320	2.80	10	17

[a] Polymerization conditions: [IB] = 0.91 M; solvent CH_2Cl_2/*n*-hexane 80/20 v/v; polymerization time 3 min. [b] Functionality at the α-end, determined by ^1H NMR spectroscopy. [c] Solvent CH_2Cl_2/*n*-hexane 60/40 v/v; polymerization time 30 min. [d] Pyridine was added: [Py] = 0.000 25 M. [e] Pyridine was added: [Py] = 0.000 45 M. [f] Reaction time 7 min. [g] No *exo*-olefin terminal group was detected.

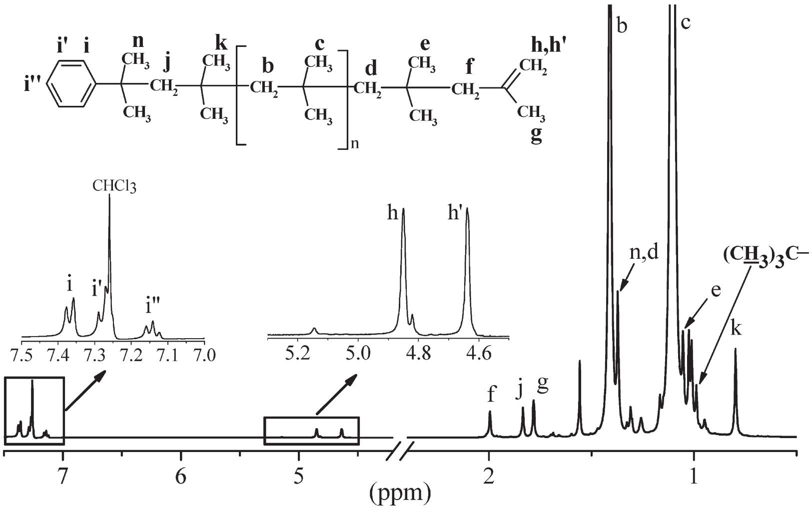


Figure 1. ^1H NMR spectrum of polyisobutylene (run 6, Table 1) obtained using the CumOH/$AlCl_3OBu_2$ initiating system at −40 °C.

chains were initiated by CumOH, indicating that protonic initiation via water or/and due to chain transfer reactions operated in the system (run 1, Table 1 and Figure S1). Higher concentration of CumOH gave rise to nearly quantitative conversion in 3 min (run 2, Table 1). The obtained polymers were of low molecular weight (M_n = 2330 g mol^{-1}) and monomodal (see, for example, Figure S2) molecular weight distribution (M_w/M_n < 1.8) as well as were characterized by high content of *exo*-olefin end groups (86%) and high functionality at the α-end (degree of initiator incorporation, F_n(Cum) = 91%).

The effect of temperature on the synthesis of highly reactive polyisobutylene using the CumOH/$AlCl_3OBu_2$ initiating system is also illustrated in Table 1. Basically, the increase in the reaction temperature from −60 to −20 °C led to the gradual decrease of monomer conversion and molecular weight and to the narrowing of molecular weight distribution down to M_w/M_n < 1.2 (Figure S3) at −20 °C. On the other hand, increasing the temperature did not influence significantly the content of *exo*-olefin end groups (runs 2, 3, and 7). Higher initiator concentration resulted in higher monomer conversion and narrower molecular weight distribution (MWD) (compare runs 3 and 6). In the absence of initiator, the cationic polymerization of isobutylene proceeded at lower reaction rate than with initiator, affording polymers with high content of vinylidene end groups (92%) and acceptable MWD (M_w/M_n = 2.25) (runs 7 and 8).

Since in some experiments we observed a low degree of initiator incorporation in the polymer chains (F_n(Cum) < 50%), i.e., competitive protonic initiation took place, we investigate the effect of pyridine as a proton trap[17] on the polymerization of isobutylene with the CumOH/$AlCl_3OBu_2$ initiating system. Basically, increasing the concentration of pyridine in the system led to a gradual decrease in molecular weight and significant narrowing in molecular weight distribution of obtained polymers (from 1.46 to 1.17) but also to the decrease of degree of initiator incorporation. In other words, the addition of pyridine resulted in the increase of the rate of chain transfer reaction (see runs 3−5, Table 1).

The structure of the obtained polyisobutylenes was studied using ^1H NMR spectroscopy and MALDI-TOF-MS. Figure 1 shows a typical ^1H NMR spectrum of a PIB obtained with the CumOH/$AlCl_3OBu_2$ initiating system.

The expansion of olefinic region (inset) shows two major signals at 4.64 and 4.85 ppm for the terminal vinylidene (*exo*-olefin) end groups. The small fraction of *endo*-olefin-terminated PIB (~3.5%) and coupled polyisobutylene chains (6.5%) are observed at 5.15 and 4.82 ppm (as a shoulder to the downfield *exo*-olefin peak at 4.85 ppm),[9,18] respectively. Importantly, there is no peak at 1.68 ppm, indicating the absence of *tert*-chloride end groups. In addition, the resonances due to the initiator residue are visible at 7.1−7.4 ppm (phenyl protons) as well as at 1.83 ppm (*j*), 1.37 ppm (*n*), and 0.8 ppm (*k*), which is consistent with earlier reported assignment.[9,19] The functionality of the α-end (F_n(Cum) = 91%), calculated as $F_n(\mathrm{Cum}) = I(\mathrm{i}'')/[I(\mathrm{h})+I(endo)]$ or $F_n(\mathrm{Cum}) = I(\mathrm{i}'')/[I(\mathrm{i}'') + I((CH_3)_3C)/9]$, is slightly lower than 100%, indicating that either chain transfer or competitive protonic initiation operates in the system. Indeed, a small peak at 0.99 ppm corresponding to a $(CH_3)_3C-$ head group is detected in the spectrum, but its content does not exceed 10%.

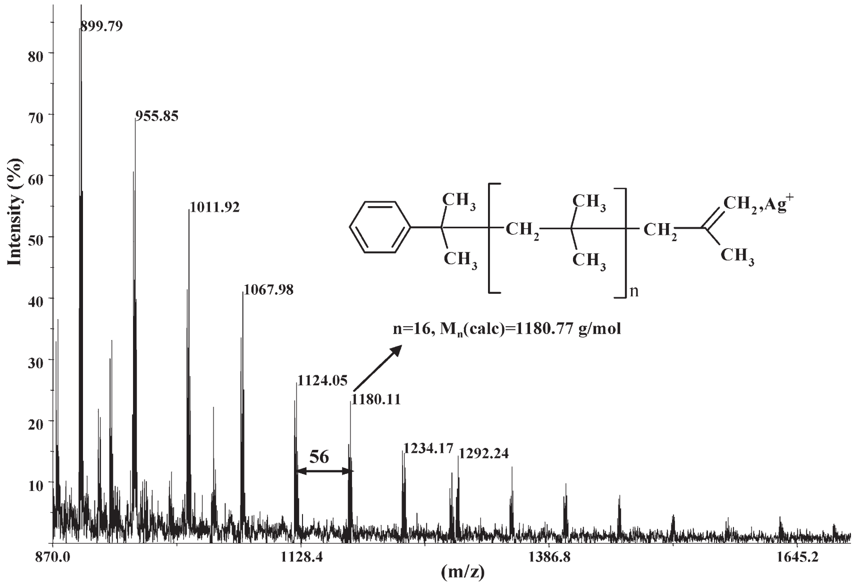
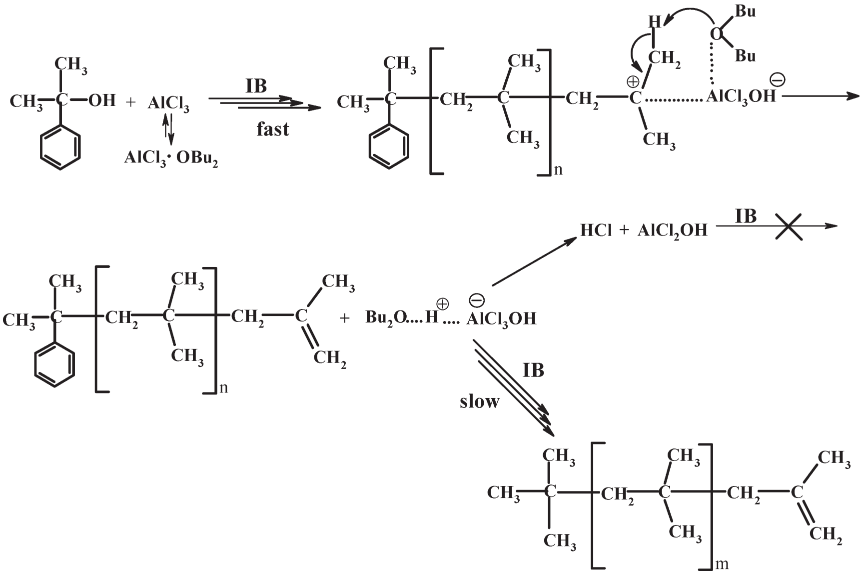


Figure 2. MALDI-TOF MS of polyisobutylene (run 6, Table 1) obtained using the CumOH/$AlCl_3OBu_2$ initiating system at −40 °C.

Scheme 2. Proposed Mechanism for Isobutylene Polymerization Using the CumOH/$AlCl_3OBu_2$ Initiating System



Recently, Harrison et al.[3] showed by means of negative ion electrospray ionization mass spectrometry (ESI-MS) of polyisobutenylsuccinic anhydride that $AlCl_3$-catalyzed polymerization of isobutylene led to the formation of polymers with the anomalous carbon numbers; i.e., the mass difference between peaks was 14 g mol^{-1}, against the 56 g mol^{-1} expected (molar mass of monomer unit). To explain such observation, it was proposed that $AlCl_3$-coinitiated cationic polymerization of isobutylene proceeds via carbocation rearrangements (hydride and CH_3− shifts) and via β-scission reactions.[3] Similar conclusions have been made based on the ^{13}C NMR spectroscopy investigations of polyisobutylene samples prepared using $AlCl_3$ as catalysts.[20] Therefore, we have investigated the structure of polyisobutylenes obtained with the CumOH/$AlCl_3OBu_2$ initiating system by MALDI-TOF-MS (Figure 2).

The MALDI-TOF-MS spectrum of a typical polyisobutylene (run 6, Table 1), given in Figure 2, shows a narrow distribution of peaks separated by 56 g mol^{-1}, corresponding to one isobutylene unit. Only one series of peaks corresponding to polymer chains cationized by silver and bearing fragment of initiator at the α-end and a double bond at the ω-end (M_n = 1180.11 g mol^{-1}) are observed in the spectrum. These data clearly indicate that the mechanism of CumOH/$AlCl_3OBu_2$-initiated cationic polymerization of isobutylene is completely different from the mechanism of conventional (industrial) $AlCl_3$-catalyzed polymerization of isobutylene.

A tentative mechanism of the isobutylene polymerization with CumOH/$AlCl_3OBu_2$ initiating system is depicted in Scheme 2.

We assume that free Lewis acid, which is generated by dissociation of $AlCl_3OBu_2$ complex, participates in the initiating and propagating steps similarly to the styrene polymerization with the 1-phenylethyl chloride/$TiCl_4$/Bu_2O[21,22] and CumOH/$AlCl_3OBu_2$[16] initiating systems in the presence of equimolar amount or excess of dibutyl ether to the Lewis acid. Basically, the polymerization of isobutylene with CumOH/$AlCl_3OBu_2$ initiating system proceeds in two stages (see Figure S1 for a typical kinetic profile). During the first stage, a fast polymerization occurs due to the initiation by cumyl alcohol followed by β-H abstraction by Bu_2O to generate double-bond-terminated PIB and $H^+AlCl_3OH^-$. The latter species either participate in a competitive initiation of the polymerization, which is considerably slower than CumOH-initiated polymerization, most probably, because of the partial trapping of protons by Bu_2O, or decompose with the formation the weak Lewis acid $AlCl_2OH$, which is inactive in the polymerization.

We also hypothesize that the predominant formation of *exo*-olefin terminal groups in our system occurs through reaction of growing carbocation with free base (Bu_2O), which is formed due to the $AlCl_3OBu_2$ complex dissociation. To confirm this assumption, the effect of different bases on the chain-end functionality of PIBs obtained during the cationic polymerization of isobutylene with CumOH/$AlCl_3$ED (ED = EtOAc, Ph_2O, no base) initiating systems has been investigated. As shown in Table 1 (runs 7, 9, and 10), the decrease of the basicity of the corresponding ED in $AlCl_3$ED complex leads to a dramatic lowering of *exo*-olefin end group content (compare Figure 1 and Figure S4): Bu_2O ($pK_a = -3.59$,[23] *exo* = 91%); EtOAc ($pK_a = -6.5$,[23] *exo* = 53%); Ph_2O ($pK_a = -6.54$,[24] no *exo*-olefin end groups). Interestingly, the polymerization of isobutylene in the presence of such weak base as Ph_2O proceeds almost in the same manner as in the base-free system, i.e., when suspension of $AlCl_3$ in CH_2Cl_2 was used as a coinitiator (see runs 9 and 11 in Table 1 and Figure S4). These results confirm our assumption that the basicity of electron donors used for the preparation of complexes with $AlCl_3$, which are soluble in organic solvents, plays a key role in the synthesis of polyisobutylenes with high content of *exo*-olefin terminal groups. The better functionality was obtained with dibutyl ether, which is characterized by moderate basicity ($pK_a = -3.59$). The use of such strong base as pyridine did not influence the content of *exo*-olefin end groups but led to the decrease of reaction rate (see runs 3−5, Table 1) due to the strong complexation with Lewis acid. Storey et al.[9] showed that considerably stronger, but sterically hindered, bases (to prevent complexation with Lewis acid) 1,2,2,6,6-pentamethylpiperidine (pK_a = 11.25) or 2-*tert*-butylpyridine (pK_a = 5.69) were also effective toward selective β-H elimination during the isobutylene polymerization with the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system. In addition, from the obtained results it is evident that the molecular weight of polymers synthesized with the CumOH/$AlCl_3OBu_2$ initiating system is controlled by the concentration of free base (Bu_2O), not by [isobutylene]/[CumOH] ratio.

The nature of counteranion, i.e., dimeric or monomeric, is believed also to strongly influence the polymerization mechanism.[25] For example, it was shown that $AlBr_3$-[26] or $RAlCl_2$-catalyzed[27] polymerization of isobutylene involved dimeric counteranions in the absence of electron donor additives or when the concentration of Lewis acid (LA) was considerably higher than concentration of ED. On the contrary, a first-order dependence on LA was observed for the cationic polymerization of styrene in the presence of equimolar concentration or excess of ED toward $TiCl_4$[22] or $AlCl_3$.[28] We are currently investigating the mechanism of the cationic polymerization of isobutylene with CumOH/$AlCl_3$ED initiating systems in details.

In conclusion, CumOH in combination with $AlCl_3OBu_2$ provides a very efficient initiating system for the synthesis of highly reactive polyisobutylenes (M_n = 1000−5000 g mol^{-1}) with rather narrow molecular weight distribution (M_w/M_n = 1.2−1.9) containing 86−95% of *exo*-olefin end groups at elevated reaction temperatures (−40 to −20 °C). The predominant formation of *exo*-olefin-terminated polyisobutylenes during the cationic isobutylene polymerization with the CumOH/$AlCl_3OBu_2$ initiating system is consistent with a selective β-H abstraction by free Bu_2O formed due to the dissociation of the $AlCl_3OBu_2$ complex. The basicity of electron donors used for the preparation of complexes with $AlCl_3$ plays a key role in the synthesis of polyisobutylenes with high content of *exo*-olefin terminal groups.

Experimental Section. *a. Materials and Methods.* Isobutylene (Aldrich, 99%) was dried in the gaseous state by passing through the column packed with $CaCl_2$. Ethyl acetate (Aldrich, 99.5%) and pyridine (Aldrich, ≥99%) were distilled twice from CaH_2 under an inert atmosphere. Diphenyl ether (Aldrich, ≥99%) was distilled from CaH_2 under reduced pressure. Size exclusion chromatography (SEC) was performed on a PL-GPC 50 integrated GPC system with two columns (PL gel, 5 μm, 300 mm, 500 and 100 Å) and one precolumn (PL gel 5 μm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Laboratories, Germany). ^1H (400 MHz) spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the residual solvent resonance. MALDI-TOF-MS was conducted using a Bruker Reflex III time-of-flight mass spectrometer (Bruker Daltonics, Billerica, MA). This instrument utilizes an attenuated nitrogen laser (337 nm), a single-stage pulsed ion extraction source, a two-stage gridless reflector, and two dual microchannel plate detectors for detection in linear and reflectron modes. The instrument was run in reflectron mode using an acceleration potential of 20 kV for all experiments. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97+%), polymer sample (10 mg/mL), and silver trifluoroacetate (10 mg/mL) (Aldrich, 98%) were prepared in THF (Aldrich, 99.9%). These solutions were then mixed in the ratio of matrix/sample/cationizing salt = 10:2:1, and 0.5 μL aliquots were applied to a MALDI sample target for analysis. The instrument was calibrated externally using polystyrene standards at the appropriate molecular weight. All mass-to-charge ratios (m/z) quoted are monoisotopic; i.e., they include the most abundant isotopes of the elements present in the corresponding ion. Other materials have been previously described.[16,29]

b. Synthesis of $AlCl_3$ Complexes. The complexes of $AlCl_3$ with different electron donors (Bu_2O, EtOAc, and Ph_2O) were prepared under an argon atmosphere in CH_2Cl_2 solution at room temperature. As a typical example, the synthesis of $AlCl_3OBu_2$ complex is given below: Bu_2O (3.8 mL, 2.25×10^{-2} mol) was added dropwise to slurry of $AlCl_3$ (3 g, 2.25×10^{-2} mol) in 18.7 mL of CH_2Cl_2 for 5−10 min. The reaction was allowed to stir for 30−60 min up to complete dissolving of $AlCl_3$ to give a solution of complex ($AlCl_3OBu_2$) in CH_2Cl_2 (1 M). The concentration of complex was determined by back-titration of Al with EDTA disodium salt by $ZnSO_4$ with diphenylthiocarbazone as an indicator.

c. Polymerization Procedures. The polymerization reactions were carried out in glass tubes under an argon atmosphere at different temperatures (from −20 to −60 °C). As an example of a typical procedure, polymerization was initiated by adding a solution of $AlCl_3OBu_2$ in CH_2Cl_2 (0.6 mL, 1 M) to a mixture of a total volume of 27.4 mL consisting of isobutylene (1.43 g, 2.55×10^{-2} mol), 2-phenyl-2-propanol (CumOH) (5×10^{-4} mol), CH_2Cl_2 (20 mL), and *n*-hexane (5 mL). After a predetermined time, 3−5 mL aliquots were withdrawn and poured into methanol. The quenched reaction mixtures were diluted by *n*-hexane, washed with 0.5 M nitric acid and deionized water to remove the aluminum−containing residues, evaporated to dryness under reduced pressure, and dried in vacuum to give the product polymers. Monomer conversions were determined gravimetrically.

Acknowledgment. The authors thank BASF SE for financial support of this research. S.K. thanks Dr. Hannah M. König and Dr. Klaus Mühlbach (BASF SE, Ludwigshafen, Germany) for their useful comments to this article and Christelle Absalon (Institut des Sciences Moléculaires-CESAMO) for MALDI-TOF analyses.

Supporting Information Available: Conversion vs time plot, SEC traces, and ^{1}H NMR spectra of polyisobutylene samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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